

## van der Waals Force, Dispersion Theory, and Singularities on Second Riemann Sheets\*

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Previous work on the long-range electromagnetic forces between neutral particles is extended to obtain a more detailed understanding of the atomic or molecular van der Waals forces within the framework of covariant dispersion theory. It is shown that the modulation of the two-photon exchange potential  $V_{2\gamma}$  from the London form  $V_{2\gamma} \sim R^{-6}$  to the Casimir-Polder form  $V_{2\gamma} \sim R^{-7}$  has an interesting dispersion-theoretic interpretation: It arises as a consequence of singularities in the momentum transfer  $t$  of the scattering amplitude  $F(s,t)$  in the physical region of  $t$  but on an unphysical Riemann sheet. The connection of the present approach with that of Casimir and Polder is explained. The one-photon exchange potential  $V_{1\gamma}$  is also studied for systems bound by either short-range or Coulomb forces. Some of the modification of the usual assumptions of dispersion theory required to deal with the latter case are described. An erroneous statement in the literature regarding  $V_{1\gamma}$  (in the static limit) is pointed out. The character of  $V_{1\gamma}$  and  $V_{2\gamma}$  arising from photon exchange between elementary particles is described and contrasted with the atomic case. Some of the advantages of a covariant approach to the problem of interatomic forces are discussed.

### I. INTRODUCTION

IN a previous paper,<sup>1</sup> the long-range electromagnetic forces acting between elementary systems or particles were studied with the help of the ideas of dispersion theory and the general principles of quantum electrodynamics. In that work, motivated by some anomalies reported in experiments involving the passage of neutral  $K$  mesons through matter, the emphasis was on the forces arising from multiple photon exchange between a neutral spinless particle such as the  $K^0$  meson and a charged particle such as the proton. An interesting byproduct of the techniques developed in FS was a simple proof of a general property of  $V_{2\gamma}(R)$ , the two-photon exchange potential acting between any two neutral spinless particles: For large separations  $R$  one has

$$V_{2\gamma}(R) \sim R^{-7}. \quad (1.1)$$

Since, for example, a hydrogen atom in its ground state may be regarded as an elementary system or particle, this result is in agreement with, and constitutes a generalization of the much earlier work of Casimir and Polder<sup>2</sup> on the van der Waals forces acting between neutral atoms. These authors considered a pair of hydrogen atoms with (infinitely heavy) protons separated by a large distance  $R$  and computed the level shift  $\Delta E^{(4)}(R)$  arising from the combined effects of the electrostatic interaction  $V_e$  between the atoms and the interaction of the electrons with the transverse radia-

tion field. They showed that for  $R \rightarrow \infty$

$$\Delta E^{(4)}(R) \sim R^{-7}. \quad (1.2)$$

This was in contrast to the result of the again much earlier and pioneering work of London,<sup>3</sup> who had considered only the level shift  $\Delta E_{cc}(R)$  arising from  $V_e$  taken in second-order perturbation theory and had found that for  $R \rightarrow \infty$ ,

$$\Delta E_{cc}(R) \sim R^{-6}. \quad (1.3)$$

The purpose of this paper is to extend the work of FS to obtain a more detailed understanding of the atomic or molecular van der Waals forces from the viewpoint of dispersion theory.

The particular problem which initiated this study is the following. The result (1.2) of CP, is, more precisely, that

$$\Delta E^{(4)}(R) \simeq C'R^{-7}, \quad (R \gg b) \quad (1.2')$$

where  $C'$  is a constant and  $b$  is of the order of the longest *wavelength* associated with excitations of the individual atoms. Thus, for hydrogen atoms,

$$b \simeq 2000a_0,$$

where  $a_0$  is the Bohr radius. The result (1.3) of London is, more precisely, that

$$\Delta E_{cc}(R) \simeq CR^{-6}, \quad (R \gg a) \quad (1.3')$$

where  $a$  is a length characterizing the *size* of the interacting systems. For hydrogen atoms, we therefore have

$$a \simeq a_0.$$

Now, as shown in CP,

$$\Delta E^{(4)}(R) = CR^{-6}g(R), \quad (1.4)$$

where  $g(R)$  is a "slowly varying" function for  $R \ll b$ ,

\* F. London, *Z. Physik* **63**, 245 (1930).

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<sup>1</sup> G. Feinberg and J. Sucher, *Phys. Rev.* **139**, B1619 (1965), henceforth referred to as FS.

<sup>2</sup> H. B. G. Casimir and D. Polder, *Phys. Rev.* **73**, 360 (1948), henceforth referred to as CP. A convenient introduction to the subject is given by E. A. Power, *Introductory Quantum Electrodynamics* (Longmans Green and Company, Ltd. London, 1964), p. 108.

with

$$\begin{aligned} g(0) &= 1, \\ g(R) &\simeq (C'/C)1/R, \quad (R \gg b) \end{aligned} \quad (1.5)$$

so that a reconciliation between (1.2') and (1.3') is

$$\Delta E^{(4)}(R) \simeq CR^{-6}, \quad (a \ll R \ll b) \quad (1.6a)$$

$$\Delta E^{(4)}(R) \simeq C'R^{-7}, \quad (R \gg b). \quad (1.6b)$$

The dispersion-theoretic interpretation of (1.6b) has already been given, but the question now arises: How can the behavior (1.6a) and more particularly the changeover to (1.6b) be understood within the context of dispersion theory? To state the answer, it is necessary to introduce some notation.

Consider the elastic scattering process

$$1+2 \rightarrow 1'+2', \quad (1.7)$$

where "1" and "2" denote neutral spinless particles with initial and final 4-momenta  $p_i$  and  $p_i'$  ( $i=1, 2$ ), respectively. Let  $F(s,t)$  denote the invariant Feynman amplitude for (1.7), with  $s$  and  $t$  the squared invariant energy and momentum transfer, respectively,

$$s = (p_1 + p_2)^2, \quad t = (p_1 - p_1')^2. \quad (1.8)$$

Two-photon exchange contributes a term  $F_{2\gamma}(s,t)$  to  $F$  which is an analytic function of  $t$  with singularities which include a branch point at  $t=0$ . As shown in FS, it follows from general principles that the discontinuity across the associated cut, taken from 0 to  $+\infty$ , behaves like  $t^2$  for  $t \gtrsim 0$ , and it is this property which leads to the asymptotic form of the two-photon exchange potential given by Eq. (1.1). The answer to the problem posed can now be stated as follows: The behavior in question can be regarded as a consequence of singularities of  $F(s,t)$  in the *physical region* of  $t$  but on an *unphysical* Riemann sheet of the function  $F(s,t)$ . This rather surprising result shows that not only can dispersion theory give insight into the nature of electrodynamic forces, but that, conversely, the study of virtual electrodynamic processes, i.e., multiple photon exchange, can illuminate some aspects of dispersion theory which are obscured when only the strong interactions are considered.

The singularities referred to occur for real values of  $t$  with  $t < 0$  and occur both as poles and as branch points. They are thus rather different from the familiar second sheet poles with  $\text{Re}t > 0$  and  $\text{Im}t < 0$ , which may be interpretable in terms of resonances if  $\text{Re}t$  and  $|\text{Im}t|$  are sufficiently large and small, respectively. A more detailed discussion is given in Secs. II and V; we want to emphasize here only that these singularities do not depend sensitively on the nature of the systems exchanged but are more or less determined by the "structure" of the particles undergoing the scattering. They are present even in the contribution to, e.g., hydrogen-hydrogen scattering arising from the exchange of, say, two  $\pi^0$  or  $\rho^0$  mesons. However, in that

case the singularity is quite far from any physical region. It is only when the cut at  $t=0$  introduced by two-photon exchange is taken into account and when the scattering systems in question are atoms that the singularity is relatively close to the physical region, as measured in terms of path length on the Riemann surface.

In the above discussion, we have emphasized the two-photon exchange force. What about the effect of single-photon exchange? This is sometimes stated to vanish identically, for atoms with  $L=0$  in the ground state, at least in the static limit. However, in fact it gives rise to a force which falls off exponentially with  $R$ . As we shall see, this is an immediate consequence of dispersion-theoretic considerations and is in agreement with what is really obtained from ordinary non-relativistic quantum mechanics. For, although the exchange of a single transverse photon is forbidden between two (infinitely heavy) hydrogen atoms each of which is in its ground state, the expectation value of the electrostatic interaction  $V_e$  is not zero in this state, contrary to the assertions made in a number of textbooks.<sup>4</sup> This fact is undoubtedly well known to many people<sup>5</sup>; we mention it here only because so many physicists have learned quantum mechanics from one of the two classics in Ref. 4.

We now outline the content of the following sections. In Sec. II, the basic ideas of the dispersion-theoretic approach to multiphoton exchange forces are first briefly reviewed; the second-sheet singularities in question are then exhibited with the aid of a simple model and their connection with the two-photon exchange potential is explained. In Sec. III the results of Sec. II are confirmed by showing that the formula for  $\Delta E^{(4)}(R)$  obtained by CP can be rewritten, with the aid of a fivefold integration by parts, in a form which makes manifest the relation of their result with that obtained from dispersion theory. In Sec. IV, the single-photon exchange potential is briefly studied and some of the modifications necessary to adapt the dispersion theory methods to cases where bound states are produced by the Coulomb force are described. Finally, Sec. V contains a summary and a discussion of the following topics: (i) comparison between the atomic and elementary particle cases, (ii) reduced diagrams and the critical role played by intermediate particles with spin, (iii) the advantages of a covariant approach in the study of photon exchange forces, and (iv) the generality of the results. Some additional considerations con-

<sup>4</sup> See, e.g., L. Pauling and E. B. Wilson, *Introduction to Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1935), p. 384. A similar discussion is given in L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1955), p. 176.

<sup>5</sup> That  $\langle V_e \rangle \neq 0$  is implicit in many publications; we thank Professor E. A. Mason and Professor L. S. Rodberg for discussion of this point. The value of  $\langle V_e \rangle$  for two hydrogen atoms is recorded in Eq. (4.12). To our surprise, we were unable to find this easily obtainable expression in the literature.

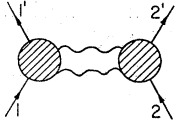


FIG. 1. General form of a Feynman diagram corresponding to the exchange of two photons between particles "1" and "2."

cerning the connection between the potential and second-sheet singularities are given in the Appendix.

## II. TWO-PHOTON EXCHANGE AND THE SECOND RIEMANN SHEET

### A. Definition of $V_{n\gamma}(R)$ , the $n$ Photon Exchange Potential

Let  $F_{n\gamma}(s,t)$  denote the contribution to the amplitude  $F(s,t)$  for process (1.7) of all Feynman diagrams which involve the exchange of precisely  $n$  photons between particles 1 and 2, each assumed to be neutral and spinless. The contribution of, for example, two-photon exchange is symbolized as in Fig. 1. We define  $F_{n\gamma}^{\text{irr}}(s,t)$  as that part of  $F_{n\gamma}(s,t)$  which comes from irreducible diagrams, i.e., those for which there is no intermediate state containing "1" and "2" only.<sup>6</sup>

Both  $F_{n\gamma}(s,t)$  and  $F_{n\gamma}^{\text{irr}}(s,t)$  are expected to be analytic functions of  $t$  with a right-hand cut starting at  $t=0$  if  $n \geq 2$ , so that we may write

$$F_{n\gamma}(s,t) = \frac{1}{\pi} \int_0^\infty \frac{\rho_{n\gamma}(s,t')}{t'-t} dt' + \dots \quad (2.1)$$

and

$$F_{n\gamma}^{\text{irr}}(s,t) = \frac{1}{\pi} \int_0^\infty \frac{\rho_{n\gamma}^{\text{irr}}(s,t')}{t'-t} dt' + \dots, \quad (2.2)$$

where  $2i\rho_{n\gamma}(s,t)$  is the discontinuity of  $F_{n\gamma}(s,t)$  across the right-hand cut and  $\rho_{n\gamma}^{\text{irr}}(s,t)$  is similarly defined. The dots in (2.1) and (2.2) represent the contribution of left-hand singularities; these correspond to exchange forces and are not of direct interest here. An effective potential may now be defined by setting  $t = -\mathbf{q}^2$ , where  $\mathbf{q}$  is the 3-vector momentum transfer in the center-of-mass (c.m.) system, and then taking the Fourier transform of the first term in (2.2) with respect to  $\mathbf{q}$ . The resulting potential will depend on  $s$ , but this dependence is expected to be rather weak for  $s$  near threshold, i.e., for  $s \gtrsim s_0$ , where

$$s_0 = (M_1 + M_2)^2,$$

and can be ignored for our purposes. Thus, using

$$\frac{1}{(2\pi)^3} \int \frac{1}{t' + \mathbf{q}^2} e^{i\mathbf{q}\cdot\mathbf{R}} d\mathbf{q} = \frac{1}{4\pi} \frac{e^{-(\sqrt{t'})R}}{R},$$

<sup>6</sup> The reducible Feynman diagrams, when written as a sum of time-ordered diagrams, contain parts which have intermediate states different in type from the initial state. These parts should really be included in  $F^{\text{irr}}(s,t)$  and hence in the definition of  $V$ , if one wishes to use  $V$  in a Schrödinger equation. However, in our problem such diagrams give rise only to short-range forces (see Sec. IV), so that we need not discuss this in detail.

we are led to define

$$V_{n\gamma}(R) = \frac{\text{const}}{R} \int_0^\infty \rho_{n\gamma}^{\text{irr}}(t) e^{-(\sqrt{t})R} dt, \quad (2.3)$$

where

$$\rho_{n\gamma}^{\text{irr}}(t) \equiv \rho_{n\gamma}^{\text{irr}}(s_0, t).$$

The constant unspecified in (2.3) is equal to  $(16\pi^2 M_1 M_2)^{-1}$  if  $F(s,t)$  is normalized so that the scattering amplitude is  $(-8\pi\sqrt{s})^{-1}F$ .

### B. Second-Sheet Singularities of $F_{2\gamma}(s,t)$

As discussed in FS, the discontinuity  $\rho_{2\gamma}(s,t)$  is given by

$$\rho_{2\gamma}(s,t) \propto \int \Gamma_{(1)\mu\nu}(q,q') \Gamma_{(2)\mu\nu}(-q, -q') \times \delta(p_1 - p_1' - q - q') d\Phi_{2\gamma}, \quad (2.4)$$

where  $\Gamma_{(i)\mu\nu}(q,q')$  is the form factor for two-photon emission by "i" and the integration is over the two-photon phase space,

$$d\Phi_{2\gamma} \propto \delta(q^2) \delta(q'^2) d^4q d^4q'.$$

The neutrality of the particles and conservation of the electromagnetic current imply that<sup>1</sup>

$$q^\mu \Gamma_{(i)\mu\nu} = q'^\nu \Gamma_{(i)\mu\nu} = 0, \quad (2.5)$$

and these relations together with a very mild assumption on the analyticity properties of  $\Gamma_{(i)}$  are sufficient to show that for  $t \sim 0$ ,

$$\rho_{2\gamma}(s_0, t) \sim t^2, \quad (2.6)$$

from which the universality of the  $R^{-7}$  behavior follows. To understand the behavior of  $V_{2\gamma}(R)$  in more detail, it is necessary to know more about  $\rho_{2\gamma}(s_0, t)$  than Eq. (2.6) and hence more about the  $\Gamma_{(i)\mu\nu}$  than Eq. (2.5).

Rather than attempt to discuss the information needed about the  $\Gamma_{(i)}$  in general terms, it is more transparent to study a simple model for the  $\Gamma_{(i)}$  which, however, contains the essence of both the mathematics and physics which comes into play here. We assume that "1" is coupled to a neutral *vector* particle "3" in such a way that the virtual transition

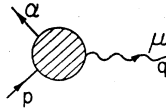
$$"1" \rightarrow "3" + \text{photon} \quad (2.7)$$

is possible. Let  $V_{(1)\alpha\mu}(q,p)$  denote the vertex function for the process (2.7) to first order in  $e$ , as symbolized in Fig. 2. There is then a contribution  $T_{(1)\mu\nu}(q,q')$  to  $\Gamma_{(1)\mu\nu}$ , corresponding to Fig. 3, which is given by

$$T_{(1)\mu\nu} \propto V_{(1)\beta\nu}(q', -p_1') V_{(1)\alpha\mu}(q, p_1) \times (g_{\beta\alpha} - p_{3\beta} p_{3\alpha} / M_3^2) (p_3^2 - M_3^2)^{-1}, \quad (2.8)$$

where  $p_3 = p_1 - q$  and  $M_3$  is the mass of particle "3." The simplest choice for  $V_{(1)\alpha\mu}(q,p)$  consistent with

FIG. 2. Symbolic representation of the vertex function for the transition described by Eq. (2.7).



current conservation and gauge invariance is<sup>7</sup>

$$V_{(1)}^{\alpha\mu}(q,p) = g(q^\alpha p^\mu - q \cdot p g^{\alpha\mu}), \quad (2.9)$$

where  $g$  may be a function of the invariants  $q^2$ ,  $p^2$ , and  $p \cdot q$ , but will be taken as a constant for simplicity. From (2.8) and (2.9) we get

$$T_{(1)}^{\mu\nu}(q',q) \propto (p_3^2 - M_3^2)^{-1} [p_1 \cdot q p_1' \cdot q' g^{\mu\nu} + \dots], \quad (2.10)$$

where only one of the eight terms in  $T_{(1)}^{\mu\nu}$  has been written explicitly. We now assume that "2" is similarly coupled to a vector particle of mass  $M_4$  and get a contribution  $T_{(2)}^{\mu\nu}$  to  $\Gamma_{(2)}^{\mu\nu}$  analogous to (2.10),

$$T_{(2)}^{\mu\nu}(-q', -q) \propto (p_4^2 - M_4^2)^{-1} \times [p_2 \cdot q p_2' \cdot q' g^{\mu\nu} + \dots], \quad (2.11)$$

where  $p_4 = p_2 + q$ . The corresponding contribution to  $\rho_{2\gamma}$  is most readily evaluated by working in the c.m. system of the crossed reaction

$$1 + \bar{1}' \rightarrow \bar{2} + 2',$$

where we may write

$$p_1 = (\frac{1}{2}\sqrt{t}, \mathbf{p}), \quad \bar{p}_1' = (\frac{1}{2}\sqrt{t}, -\mathbf{p}), \\ \bar{p}_2 = (\frac{1}{2}\sqrt{t}, -\mathbf{p}'), \quad p_2' = (\frac{1}{2}\sqrt{t}, \mathbf{p}'),$$

and, on the mass shell of the photons,

$$q = \frac{1}{2}\sqrt{t}(1, \hat{q}), \quad q' = \frac{1}{2}\sqrt{t}(1, -\hat{q}).$$

Using (2.4), (2.10), and (2.11), we then get a contribution to  $\rho_{2\gamma}$  proportional to

$$I = I^2 \int \frac{N}{D} d\hat{q}, \quad (2.12)$$

where  $N = N(t, x_1, x_2)$  is a low-order polynomial in  $x_1 = \hat{p} \cdot \hat{q}$  and  $x_2 = \hat{p}' \cdot \hat{q}$  with coefficients which are simple algebraic functions of  $t$  [polynomials in  $t$ ,  $\sqrt{t}$ , and  $(t - 4M_i^2)^{1/2}$ ,  $i = 1, 2$ ], while

$$D \equiv (p_3^2 - M_3^2)(p_4^2 - M_4^2) = D_1(t, x_1)D_2(t, -x_2),$$

with

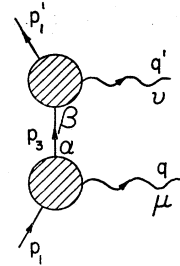
$$D_i(t, y) = M_i^2 - M_{i+2}^2 - \frac{1}{2}t + y(\frac{1}{4}t^2 - M_i^2 t)^{1/2}.$$

It follows from (2.12) that  $I(t)$  is an analytic function of  $t$  whose dynamical singularities include those arising from the vanishing of the  $D_i(t, x_i)$  at the endpoints  $x_i = \pm 1$ . The condition

$$D_i(t, \pm 1) = 0$$

<sup>7</sup> Equation (2.9) corresponds to an interaction Lagrangian  $L \propto \phi(\partial^\mu \chi^\nu - \partial^\nu \chi^\mu)F_{\mu\nu}$ , where  $\phi$  and  $\chi^\mu$  are the spin-0 and spin-1 fields associated with particles "1" and "3," respectively, and  $F_{\mu\nu}$  is the electromagnetic field tensor.

FIG. 3. Lowest-order diagram corresponding to two-photon emission by "1," arising from the vertex displayed in Fig. 2.



yields as singularities the points  $t = \tau_1$  and  $t = \tau_2$ , where

$$\tau_1 = -(M_3^2 - M_1^2)^2 / M_3^2, \quad (2.13) \\ \tau_2 = -(M_4^2 - M_2^2)^2 / M_4^2.$$

The integrations in (2.12) can be carried out explicitly, but we need not record the result. We remark only that the singularities (2.13) are logarithmic if  $\tau_1 \neq \tau_2$ , while if  $\tau_1 = \tau_2$ ,  $I(t)$  has both a pole and a logarithmic branchpoint at  $t = \tau_1 = \tau_2$ .

Now let  $F_{II}(s, t)$  denote the analytic continuation of  $F(s, t)$  obtained by starting in the upper-half  $t$  plane and passing through the cut starting at  $t = 0$ , below the next real singularity of  $F(s, t)$  at  $t = t_1 > 0$ . Let  $\rho_I(s, t)$  denote the analytic continuation into the complex  $t$  plane of the function defined by

$$\rho(s, t) \equiv [F(s, t + i0) - F(s, t - i0)] / 2i, \quad 0 \leq t < t_1. \quad (2.14)$$

Then

$$F_{II}(s, t) = F(s, t) + 2i\rho_I(s, t).$$

It follows that  $F_{II}(s, t)$  is in general singular at points  $t$  which are singularities of  $\rho_I$ , and certainly so at points  $t$  for which  $F(s, t)$  is regular and  $\rho_I$  singular.

In the model under consideration, with exchange of more than two photons neglected,  $\rho_I(s_0, t) \propto I(t)$ , Eq. (2.12), so that  $\tau_1$  and  $\tau_2$  are singularities of  $F_{II}(s_0, t)$  and hence *second-sheet* singularities of  $F(s_0, t)$ . These singularities are also singularities of  $\rho_{2\gamma}^{\text{irr}}(s_0, t)$ , since Fig. 4 represents an irreducible diagram, and can be regarded as *responsible* for the modulation from (1.6b) to (1.6a) in the following sense: If  $\rho_I(t)$  were analytic in the entire disk  $|t| < t_1$ , then  $V_{2\gamma}(t)$  could be written as a sum of terms involving inverse powers of  $R$ , the lowest power being  $1/R^7$ , and terms involving lower powers, such as  $1/R^6$ , multiplied by  $\exp(-R\sqrt{t_1})$  [see Eq. (A6)]. It follows that in this case one cannot expect a dominant  $1/R^6$  behavior in an appreciable interval. Of course, the existence of the singularities does not by itself assure such behavior. However, a

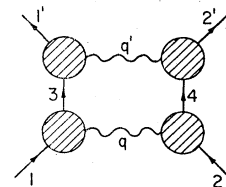


FIG. 4. Simplest irreducible scattering diagram with exchange of two photons.

more detailed analysis of Eq. (2.12) shows that if

$$\tau \equiv \min_{i=1,2}(-\tau_i) \ll t_1,$$

then  $I(t)$  is dominated by a term of the form

$$t^2 [\tan^{-1}(t/\tau)^{1/2}] / (t/\tau)^{1/2}$$

for  $\tau \ll t \ll t_1$ . As shown in the Appendix, this is just right to ensure the validity of a  $1/R^6$  approximation in a region  $(t_1)^{-1/2} \ll R \ll (\tau)^{-1/2}$ . In the atomic case, this corresponds roughly to an interval  $(a_0, \alpha^{-1}a_0)$ , as expected from the discussion in Sec. I. The connection between the above analysis and the nonrelativistic calculation of CP is considered in Sec. III.

### III. CONNECTION BETWEEN THE CASIMIR-POLDER FORMULA AND DISPERSION THEORY

The result of CP for  $\Delta E^{(4)}(R)$  (defined in Sec. I) may be written in the form

$$\Delta E^{(4)}(R) = -\frac{4}{\pi \hbar c} \sum_{m,n} k_m k_n q_m^2 q_n^2 I_{m,n}(R), \quad (3.1)$$

where

$$I_{m,n}(R) = \int_0^\infty \frac{du u^4 e^{-2uR}}{(u^2 + k_m^2)(u^2 + k_n^2) R^2} \times \left( 1 + \frac{2}{uR} + \frac{5}{u^2 R^2} + \frac{6}{u^3 R^3} + \frac{3}{u^4 R^4} \right). \quad (3.2)$$

Here  $k_m = (E_m - E_0)/\hbar c$  is the wave number of the photon emitted when one of the atoms undergoes a transition from a state of energy  $E_m$  to the ground state of energy  $E_0$ , and  $q^2$  is equal to the sum over a degenerate level of the squares of the matrix element of the electric dipole moment operator  $ez$ , taken between the ground state and the states of energy  $E_m$  (necessarily  $p$  waves).

Equation (3.2) can be brought into the form (2.3), exhibiting the potential as  $R^{-1}$  times a Laplace-like transform of the discontinuity of the scattering amplitude. This is achieved by carrying out repeated integration by parts on the coefficients of  $e^{-2uR}$  to remove the higher inverse powers of  $R$  in (3.2). With the change of variable  $4u^2 = t$  this procedure yields, after a lengthy but straightforward computation,

$$I_{m,n}(R) = \frac{1}{R} \int_0^\infty \rho_{m,n}(t) e^{-(\sqrt{t})R} dt, \quad (3.2')$$

where for  $k_m \neq k_n$ ,

$$\rho_{m,n}(t) = \frac{-1}{2(k_m^2 - k_n^2)} \left\{ \left[ \left( \frac{t\sqrt{t}}{8k_m} + \frac{1}{2}\sqrt{tk_m} + \frac{k_m^3}{\sqrt{t}} \right) \times \left( \tan^{-1} \frac{\sqrt{t}}{2k_m} \right) - \frac{1}{2}k_m^2 \right] - [k_m \rightarrow k_n] \right\}, \quad (3.3)$$

and for  $k_n = k_m = k$ ,

$$\rho_{m,m}(t) = \frac{1}{4} \left[ \left( \frac{t\sqrt{t}}{8k^3} - \frac{\sqrt{t}}{2k} - \frac{3k}{\sqrt{t}} \right) \left( \tan^{-1} \frac{\sqrt{t}}{2k} \right) + \frac{2k^2}{t+4k^2} + \frac{t}{4k^2} + 1 \right]. \quad (3.4)$$

One can easily check that  $\rho_{m,n} \sim t^2$  for  $t \rightarrow 0$ , as expected from the discussion in Sec. I. Furthermore, since

$$\tan^{-1} z = \frac{1}{2}i \ln \left[ \frac{i+z}{i-z} \right],$$

(3.3) shows that  $\rho_{m,n}$  is an analytic function of  $t$  whose only singularities are a pair of logarithmic branch points on the real negative axis at

$$t = -4k_m^2, \quad t = -4k_n^2. \quad (3.5)$$

In the case  $m=n$ , we have *both* a pole and a logarithmic branch point as seen from (3.4).

We can compare these results with those obtained in Sec. II for the singularities of  $I(t)$  [Eq. (2.13)]. We identify particles "1" and "2" with hydrogen atoms in their ground state and particles "3" and "4" with bound  $p$ -wave excited states of these atoms,  $\phi_m$  and  $\phi_n$ , respectively. Then (in units with  $\hbar=c=1$ )  $M_3 = M_H + k_m$ ,  $M_4 = M_H + k_n$ , where  $M_H = M_1 = M_2$  is the mass of the H atom, so that

$$\tau_1 \rightarrow -k_m^2 (2M_H + k_m)^2 / (M_H + k_m)^2.$$

Since  $k_m/M_H \sim \alpha^2 m_e/M_H \ll 1$ , we have

$$\tau_1 \simeq -4k_m^2, \quad \tau_2 \simeq -4k_n^2, \quad (3.6)$$

in agreement with (3.5).

It is interesting to note that  $I_{m,n}(R)$  may be expressed completely in terms of the cosine-integral and sine-integral functions  $\text{Ci}(x)$  and  $\text{Si}(x)$ , which are extensively tabulated. In the case where both atoms are excited to the same state the result is

$$I_{m,m}(R) = (3\pi/4k^3)(1/R^6)g(\beta), \quad (3.7)$$

where

$$g(\beta) = (4/3\pi) \left[ \frac{3}{2}\beta - \frac{1}{6}\beta^3 + (\text{Ci}\beta \sin\beta - \text{si}\beta \cos\beta) \times \left( \frac{3}{2} - \frac{7}{8}\beta^2 + \frac{1}{32}\beta^4 \right) + (\text{Ci}\beta \cos\beta + \text{si}\beta \sin\beta) \times \left( -\frac{3}{2}\beta + \frac{3}{8}\beta^3 - \frac{1}{32}\beta^5 \right) \right], \quad (3.8)$$

with  $\beta = 2kR$ , and  $\text{si}\beta = \text{Si}\beta - \frac{1}{2}\pi$ .

It is easy to see that  $g(\beta)$  is in fact an analytic function of  $\beta$  whose only singularity is a logarithmic branch point at  $\beta=0$ .<sup>8</sup>

<sup>8</sup> The form of  $g(\beta)$  shows, incidentally, that an expansion of the two-photon potential in inverse powers of  $R$  cannot converge for large  $R$ , and so can at best be an asymptotic expansion. Thus, even if exponential parts of the full potential, such as those arising from one-photon exchange, are included explicitly, the full potential is unlikely to permit a convergent expansion in inverse powers of  $R$ . This observation reinforces some remarks of J. O. Hirschfelder, in *Perturbation Theory and Its Applications in Quantum Mechanics* (John Wiley & Sons, Inc., New York, 1966), p. 21.

From the asymptotic forms of  $Ci\beta$  and  $Si\beta$  one finds, for  $\beta \ll 1$ ,

$$g(\beta) = 1 - \frac{1}{12}\beta^2 + \beta^3/12\pi - 7\beta^4/48 + (11\beta^5/90\pi) \ln\beta + O(\beta^6), \quad (3.9)$$

and as already given by CP, for  $\beta \rightarrow \infty$ ,

$$g(\beta) \sim 46/3\pi\beta. \quad (3.10)$$

$g(\beta)$  differs from unity by less than 0.1% for  $\beta < 0.1$ . This corresponds to  $R < 18a_0$  for the contribution of the  $(1s, 1s) \rightarrow (2p, 2p)$  transition for hydrogen atoms ( $k = 3\alpha/8a_0$ ). The departure of  $g(\beta)$  from unity begins to exceed 10% or so for  $\beta \gtrsim 1$ . The asymptotic form (3.10) becomes a good approximation for  $\beta > 10$ , corresponding to  $R > 1800a_0$  for the same transition. There is thus a rather large domain in which neither (1.6a) nor (1.6b) is a very good approximation.<sup>9</sup>

#### IV. SINGLE-PHOTON-EXCHANGE POTENTIAL

The dispersion-theoretic treatment of the one-photon exchange force between neutral spinless particles is very simple but has some interesting aspects. The matrix element for one-photon exchange is proportional to

$$F_{1\gamma} = g_{\mu\nu}\Gamma_{(1)}^\mu(q, p_1)\Gamma_{(2)}^\nu(-q, p_2)/t,$$

where  $\Gamma_{(i)}^\mu(q, p)$  is the vertex function for single-photon emission by particle "i." The general form of  $\Gamma_{(i)}^\mu$  is<sup>1</sup> (with  $P = p' + p$ ,  $q = p' - p$ )

$$\Gamma_{(i)}^\mu(q, p) = g_i(q^2)[-q \cdot P q^\mu + q^2 P^\mu],$$

where  $g_i(q^2)q^2$  is the charge form factor of "i." Since  $q_\mu\Gamma_{(1)}^\mu = 0$ , and on the mass shell  $(p_1 + p_1') \cdot (p_2 + p_2') = 2s - 2M_1^2 - 2M_2^2 + t$ , we get for  $s = s_0 \equiv (M_1 + M_2)^2$ ,

$$F_{1\gamma}(s_0, t) = g_1(t)g_2(t)t(4M_1M_2 + t).$$

It follows that the analyticity properties of  $F_{1\gamma}$  are determined by

$$g_{12}(t) = g_1(t)g_2(t).$$

If "i" is a "pure" hadron (massive particle with zero lepton number), then  $g_i(t)$  is expected to be an analytic function of  $t$  with a right-hand cut starting at  $t = t_0^{(i)} > 0$ . (In the absence of anomalous thresholds,  $\sqrt{t_0^{(i)}}$  is equal to the rest mass of the lightest charged-particle-antiparticle pair coupled to "i.") It follows that if, say,  $t_0^{(1)} < t_0^{(2)}$  then, using square brackets to denote the discontinuity across the cut,

$$[g_{12}(t)] = [g_1(t)]g_2(t), \quad t_0^{(1)} \leq t < t_0^{(2)}$$

<sup>9</sup> After this work was completed, we became aware of a paper by W. J. Meath and J. O. Hirschfelder [J. Chem. Phys. 44, 3210 (1966)], in which the CP integral (3.2) is also evaluated explicitly for the  $(1s, 1s) \rightarrow (2p, 2p)$  excitation in hydrogen. Our Eq. (3.8) is in agreement with the result of these authors, who give an extensive discussion of  $g(\beta)$ , especially with regard to the numerical accuracy of asymptotic formulas such as (3.10). We thank Professor G. Feinberg for bringing this work to our attention.

so that if  $[g_i(t)]$  is analytic at  $t = t_0^{(i)}$ , so is  $\rho_{1\gamma}(t)$ . For  $\rho_{1\gamma}(t_0) \neq 0$ , we then get from (2.3), for  $R \rightarrow \infty$ ,

$$V_{1\gamma}(R) \sim [\exp(-R\sqrt{t_0^{(1)}})]/R^2. \quad (4.1)$$

However, if "1" and "2" are identical [ $g_1(t) = g_2(t) \equiv g(t)$  and  $t_0^{(1)} = t_0^{(2)} \equiv t_0$ ], then  $g_{12}(t) \rightarrow g^2(t)$ , which is singular at  $t = t_0$  if  $[g(t)]$  is regular at  $t_0$ . If  $t_0$  is an anomalous threshold, e.g., if "1" and "2" are atoms, then  $g(t) \sim \ln[(t - t_0)/M_0^2]$ , so that<sup>10</sup>

$$[g^2(t)] \sim -4\pi i \ln[(t - t_0)/M_0^2] + 4\pi^2.$$

Thus the leading term in  $V_{1\gamma}$  arises from an integral of the type

$$\frac{1}{R} \int_{t_0}^{\infty} \ln[(t - t_0)/M_0^2] e^{-\sqrt{t}R} dt, \quad (4.2)$$

whose asymptotic form is proportional, with  $R_0 = M_0^{-1}$ , to

$$(1/R^2) \ln(R/R_0) e^{-\sqrt{t_0}R}. \quad (4.3)$$

It is amusing that the identity of the two particles thus has a *dynamical* consequence for the one-photon exchange potential in the sense that the logarithmic factor is present only in this case.

For the case of atom-atom scattering,  $t_0 \approx 4\bar{p}^2$ , where  $\bar{p}$  is the mean momentum of an electron. Thus  $\sqrt{t_0} \approx 2a_0^{-1}$  for hydrogen and  $V_{1\gamma}$  becomes small very rapidly for  $R \geq a_0$ . However, (4.3) is, in fact, not fully applicable to atom-atom scattering, as we shall now see.

Let us compare the result (4.3) with that obtained by direct evaluation of  $\langle V_e \rangle$ , where  $V_e$  is the electrostatic interaction between two H atoms separated by  $R$ :

$$V_e = \frac{e^2}{R} + \frac{e^2}{|\mathbf{R} + \mathbf{r}_1 - \mathbf{r}_2|} - \frac{e^2}{|\mathbf{R} + \mathbf{r}_1|} - \frac{e^2}{|\mathbf{R} - \mathbf{r}_2|}.$$

A short calculation yields, for  $R \rightarrow \infty$ ,

$$\langle V_e \rangle \sim -(e^2/6a_0^3)R^2 e^{-2R/a_0}, \quad (4.4)$$

in disagreement with (4.3). The source of the discrepancy is not far to seek. It arises from the fact that we have used *hydrogenic* wave functions,

$$\phi(r) \sim N e^{-Kr}, \quad (4.5a)$$

in the evaluation of  $\langle V_e \rangle$ . Had we used a bound-state wave function appropriate for binding by a short-range force, in which case, for large  $r$ ,

$$\phi(r) \sim N' e^{-Kr/r}, \quad (4.5b)$$

we would have obtained precisely the result (4.3) for  $\langle V_e \rangle$  as  $R \rightarrow \infty$ .

<sup>10</sup>  $M_0$  is a constant with the dimension of a mass. The general form of  $g(t)$  is  $A(t) \ln[(t - t_0)/M_0^2] + B(t)$ , where  $A(t)$  and  $B(t)$  are analytic at  $t = t_0$ , so that the precise value of  $M_0$  depends on how  $B(t)$  is defined.

The moral is that some of the usual assumptions of dispersion theory must be modified when the binding is caused by the long-range Coulomb force. A simple way to see what is going on is to regard the charge form factor  $G(q^2) = q^2 g(q^2)$  of a neutral particle as the Fourier transform of a charge density  $\rho_{\text{ch}}(\mathbf{r})$ , via

$$G(-q^2) = \int e^{i\mathbf{q}\cdot\mathbf{r}} \rho_{\text{ch}}(\mathbf{r}) d\mathbf{r}, \quad (4.6)$$

and to consider two simple models for the density. In either case we picture the particle as corresponding to an  $s$ -wave bound state of a pair of oppositely charged particles. For simplicity, the positively charged particle is taken to have infinite mass. Then

$$\rho_{\text{ch}}(\mathbf{r}) = e[\delta(\mathbf{r}) - \phi^2(\mathbf{r})], \quad (4.7)$$

where  $\phi(\mathbf{r})$  is the wave function of the light particle of mass  $m$ . If the binding potential behaves asymptotically as  $r^{-1}$ , (4.5a) holds, whereas for a short-range binding force (4.5b) holds for large  $r$ . We thus consider for  $\phi(\mathbf{r})$  the two cases (4.5a) and (4.5b), corresponding, respectively, to the extreme cases of a pure Coulomb binding force and a short-range binding force in the zero effective-range approximation. Here  $N$  and  $N'$  are normalization constants and  $-K^2/2m$  is the binding energy. Correspondingly, we get from (4.5a), (4.5b), (4.6), and (4.7)

$$G(t) = 1 - (2K)^4 / (4K^2 - t)^2 \quad (4.8a)$$

and

$$G(t) = 1 - \frac{\tan^{-1}[(\sqrt{-t})/2K]}{(\sqrt{-t})/2K}. \quad (4.8b)$$

Thus in case (b) the charge form factor, and hence the one-photon exchange amplitude  $G^2(t)/t$ , has the analyticity properties assumed in the discussion leading to Eq. (4.3), with  $t_0 = 4K^2$ . In case (a), however,  $G(t)$  has a (second-order) pole rather than a logarithmic branch point at  $t = t_0$ , so that the simple-minded discussion in terms of the properties of the spectral function appears to break down.

The case of a Coulomb binding force can, nevertheless, be included in the dispersion-theory framework: it is only necessary to permit the spectral function to contain *derivatives* of the Dirac delta function. To see this, let us consider the specific case at hand:

$$F_{1\gamma} = \text{const}[G^2(t)/t], \quad (4.9)$$

with  $G(t)$  given by Eq. (4.8a). The partial fraction decomposition of (4.9) is

$$F_{1\gamma} = (\text{const}) \sum_{n=1}^4 C_n (4K^2 - t)^{-n}, \quad (4.10)$$

where  $C_1 = -1$ ,  $C_2 = -(2K)^2$ ,  $C_3 = (2K)^4$ , and  $C_4 = (2K)^6$ .

Since

$$\int \frac{\delta^{(n)}(t' - \tau) dt'}{t' - t} = \frac{n!}{(\tau - t)^{n+1}}, \quad (4.11)$$

we may infer from (4.10) and (4.11) that

$$\rho_{1\gamma}(t) = (\text{const}) \pi \sum_{n=1}^4 \frac{C_n}{(n-1)!} \delta^{(n-1)}(t - 4K^2).$$

The resulting potential is then given, using (2.3) and correct normalization, by

$$V_{1\gamma}(R) = \frac{e^2}{R} \sum_{n=1}^4 \frac{C_n}{(n-1)!} \left( \frac{\partial^{n-1}}{\partial t^{n-1}} e^{-\sqrt{t}R} \right) \Big|_{t=4K^2}. \quad (4.12)$$

The leading term for  $R \rightarrow \infty$  comes from  $n=4$  and is readily seen to be the same as given by (4.4). Of course, (4.12) could also be obtained by direct computation of the Fourier transform of  $F_{1\gamma}(t)$ .

To conclude this section, we remark that the argument that  $V_{1\gamma}(R)$  [Eq. (4.12)] is zero<sup>4</sup> is fallacious because although it is true that each term in the multipole expansion of  $V_e$ , in inverse powers of  $R$ , has zero matrix element in the ground state of two hydrogen atoms, the expansion of  $V_e$  does not converge for, e.g.,  $r_1 + r_2 > 2R$ . Consequently, the sum of the matrix elements of the individual terms, though convergent, need not and in this case does not represent the value of  $\langle V_e \rangle$ . No matter how large  $R$  is, the overlap of the atomic charge distributions gives a nonzero contribution to  $\langle V_e \rangle$ .

## V. SUMMARY AND DISCUSSION

### A. Summary

We have seen that the behavior of the potential arising from two-photon exchange between neutral spinless systems has an interesting interpretation from the viewpoint of dispersion theory.

In Sec. II we studied the contribution to the two-photon exchange amplitude  $F_{2\gamma}(s, t)$  arising from the irreducible Feynman diagram shown in Fig. 4 in which the intermediate particles "3" and "4" have spin 1. It was shown that the corresponding amplitude has singularities on the Riemann sheet reached through the cut at  $t=0$ , at the points  $\tau_1$  and  $\tau_2$  [Eq. (2.13)]. Although a model was used, the existence of such singularities is expected on quite general grounds, as will be emphasized below.

In Sec. III it was demonstrated that in the case of atom-atom scattering these singularities are responsible for the changeover from the  $R^{-7}$  behavior to the  $R^{-6}$  behavior. For simplicity this demonstration was based on the CP formula (3.1), suitably transformed to facilitate comparison with covariant dispersion theory [Eqs. (3.2) and (3.3)]. This had the advantage of further exhibiting the connection of the present ap-

proach with the nonrelativistic calculation of CP. However, as would be expected, the conclusion is in fact independent of any such comparison (see the Appendix). Also, in this section the modulation function  $g(2kR)$  was exhibited in terms of well-known functions [Eq. (3.8)] and some of its properties were discussed.

In Sec. IV, the dispersion theory of  $V_{1\gamma}(R)$  was considered and the asymptotic form of  $V_{1\gamma}(R)$  was obtained both for systems bound by short-range forces [Eq. (4.3)] and by Coulomb forces [Eq. (4.4)]. Some of the modifications of the usual assumptions of dispersion theory which permit one to deal with systems bound by Coulomb forces were described, including the necessity of allowing derivatives of the delta function to occur in the spectral function. The fallacy in the argument that  $V_{1\gamma}(R) \equiv 0$  in the static limit was explained.

## B. Discussion

We now turn to a discussion of a number of points related to the preceding part of this paper. First, we describe the difference between the character of the two-photon exchange forces in the case of elementary particles and atoms. Next, we explain why an appeal to the method of reduced diagrams for location of the singularities (2.13) would have been insufficient and, in this connection, why it is necessary to allow the intermediate particles to have spin. We then discuss some of the theoretical advantages of a covariant approach to interatomic forces and consider the question of the generality of the results obtained. Finally, we list a number of related problems which seem to merit further investigation.

### 1. Comparison between the Atomic and Elementary Particle Cases

The distinction between the behavior of  $V_{2\gamma}(R)$  in the case of two neutral elementary particles and in the case of two atoms is best summarized by the following statement. In both cases  $V_{2\gamma} \sim R^{-7}$  for large  $R$ , but in the first case there is no appreciable region of validity for the approximation  $V_{2\gamma} \simeq CR^{-6}$ . This is a consequence of the fact that the lowest excitation energy of a strongly interacting "elementary" particle (not a molecule, atom, or nucleus) is  $\sim m_\pi$ , so that the associated wavelength is  $\sim m_\pi^{-1}$ , which is of the same order of magnitude as the length associated with the size of the particle.

With regard to the second-sheet singularities [Eq. (2.13)], in the elementary-particle case these are located at  $t \sim -4m_\pi^2$  or so and hence are as far from  $t=0$  as the right-hand normal threshold singularity at  $t=4m_\pi^2$ , arising from  $1+\bar{1} \rightarrow \pi+\pi$ . The latter gives rise to terms in  $V_{2\gamma}(R)$  which fall off exponentially, but at distances at which the second-sheet singularities make themselves felt ( $R$  not much larger than  $m_\pi^{-1}$ ) such terms are not small relative to the  $R^{-6}$  type

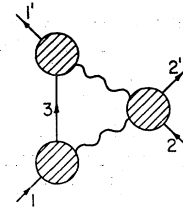


Fig. 5. A reduced diagram arising from Fig. 4.

terms. Moreover,  $V_{1\gamma}(R)$  is not small compared to  $V_{2\gamma}(R)$  in this region.

It is clear that the existence of an appreciable domain of validity for the London potential [Eq. (1.3)] in the case of atoms is directly related to the smallness of the fine-structure constant. However,  $V_{1\gamma}(R)$  is negligible relative to  $V_{2\gamma}(R)$  for  $R$  large compared to the size of the interacting systems in both the atomic and elementary-particle cases.<sup>11</sup>

### 2. Reduced Diagrams and the Role of Spin

The location of the singularities [Eq. (2.13)] can be obtained much more simply than in Sec. II by application of the Landau-Björken<sup>12</sup> rules to the reduced diagram shown in Fig. 5. For clarity we first imagine that the photon has a small mass  $M_\gamma$ . The condition for a singularity,  $\det(q_i \cdot q_j) = 0$ , with  $q_i$  the momenta of the internal lines, then implies that

$$t = -[M_1^2 - (M_3 + M_\gamma)^2][M_1^2 - (M_3 - M_\gamma)^2] / M_3^2. \quad (5.1)$$

If  $M_3^2 + M_\gamma^2 < M_1^2$ , then Eq. (5.1) corresponds to an anomalous threshold, at a positive value of  $t$  if  $M_1$  is stable. If, instead,  $M_3^2 + M_\gamma^2 > M_1^2$ , the right-hand side of Eq. (5.1) is negative and we seem to get a singularity in the physical region of process (1.7). In fact, however, under this circumstance some of the Feynman parameters associated with Fig. 5 are not positive, so that the singularity (5.1) must be on a Riemann sheet different from the physical sheet. This is in agreement with the explicit calculations of Sec. II, and, indeed, if we let  $M_\gamma \rightarrow 0$  in Eq. (5.1) we recover (2.13).

Since the rules for finding (Landau-type) singularities of Feynman diagrams are independent of particle spins (which affect only the numerator in a Feynman

<sup>11</sup> In FS it was speculated that the modulation from  $1/R^6$  to  $1/R^7$ , in the case of hydrogen, is effected by the presence of an exponential  $\exp(-\alpha R/a_0)$  in the expression for  $V_{2\gamma}(R)$ . This incorrect suggestion arose out of a careless use of excitation energies rather than mean momenta in determining the location of anomalous thresholds on the physical sheet of  $F(s_0, t)$ . In elementary-particle scattering these two quantities are normally of the same order of magnitude but in the atomic case they differ by a factor of  $\alpha$ . The excitation energies do play their role in determining the nearby second-sheet singularities, as we have seen.

<sup>12</sup> An excellent introduction to these rules is to be found in J. D. Björken and S. D. Drell, *Relativistic Quantum Fields* (McGraw-Hill Book Company, Inc., New York, 1965). For a comprehensive discussion of analytic properties of Feynman diagrams see R. J. Eden, P. V. Landshoff, D. I. Olive, and J. C. Polkinghorne, *The Analytic S-Matrix* (Cambridge University Press, New York, 1966).



integral), it may be asked why it was necessary to consider "3" and "4" with nonzero spin. The answer is that although spin can usually be ignored in considering analyticity properties of Feynman integrals, this is *not* true for the case at hand. If, say, "3" has spin zero, the Feynman integral corresponding to Fig. 4 is not singular at  $t=0$ , appearance to the contrary. In that case, the general form of the vertex function is, as in the case where "3" is identical with "1,"

$$V_\mu = g(q^2)(-q \cdot P q_\mu + q^2 P_\mu) \quad (\text{with } P = p + p'),$$

where  $g(q^2)q^2$  is a transition charge form factor. Using Eq. (2.5), one finds that the Feynman integral associated with successive photon emission via  $V_\mu$  (see Fig. 5) has an integrand proportional to

$$(\hat{p}_s^2 - M_s^2)^{-1} P_{1\mu} P_{1\nu}' \Gamma_{(2)}^{\mu\nu}(q, q'; P_2) g(q^2) g(q'^2);$$

the photon propagators have been cancelled by the coefficients  $q^2$  and  $q'^2$  of  $P_{1\mu}$  and  $P_{1\nu}'$ . As a consequence, the amplitude is analytic at  $t=0$  and the nearest singularities are those associated with the singularities of  $\Gamma_{(2)}$  and  $g(q^2)$ .<sup>13</sup>

The fact that intermediate spin-zero particles do not contribute to the long-range part of  $V_{2\gamma}(R)$  has a simple analog in the calculation of  $\Delta E^{(4)}(R)$  in nonrelativistic quantum mechanics, say, for two hydrogen atoms. If we consider  $\Delta E_{cc}(R)$ , the shift arising from  $V_c$  in second-order perturbation theory, it is easy to verify that the contribution of intermediate states in which one of the atoms is in an excited  $s$  state decreases more rapidly than any inverse power of  $R$ . (In the dipole approximation such states contribute zero to  $\Delta E_{cc}$ .) Our choice of spin-1 intermediate particles in Sec. II was made in order to facilitate comparison with the work CP. In Ref. 2 both  $V_c$  and the interaction of the electrons with the radiation field were treated in dipole approximation. As a consequence,  $\Delta E^{(4)}(R)$  received nonzero contributions *only* from excited  $p$  states for either atom. Such states are, of course, nonrelativistic analogs of vector particles; we note in passing that the choice Eq. (2.9) for  $V_{\alpha\mu}$  is such that in the nonrelativistic limit it just reduces to the amplitude for photon emission by an atom making a transition from an  $s$  state to a  $p$  state.

### 3. Advantages of a Covariant Approach

We would like to stress several advantages of the covariant dispersion-theory approach to the problem of electromagnetic forces between neutral systems. (i) Relativistic corrections to the values of such quantities as  $C$  and  $C'$  [Eqs. (1.2') and (1.3')] are likely to be small for most cases of interest, at the present level of

<sup>13</sup> This result could have been anticipated: If we identify "3" with "1" and "4" with "2" we are dealing with an iteration of single-photon exchange. Since single-photon exchange gives rise to a short-range force (see Sec. IV), its iteration should also give rise to such a force.

experimental accuracy. However, from a purely theoretical point of view, the covariant approach has the virtue of showing that these quantities have quite general physical significance and that they may be given sharp definitions in a wide class of Lorentz-invariant theories. That this should be so was not *a priori* clear since these quantities were first introduced and defined within the framework of nonrelativistic quantum mechanics. The work of FS and of the present paper shows how such quantities may be defined solely in terms of concepts associated with the on-shell invariant scattering amplitude  $F(s, t)$ . (ii) At the same time, a path is indicated for the calculation of these quantities if a case should arise in which either nonrelativistic approximations are invalid or relativistic corrections are not negligible. Although this possibility seems academic at the moment, this may not always be the case. (iii) More generally, the dispersion-theory approach may suggest useful new approximation procedures in the computation of atomic-scattering processes, as it has in elementary-particle scattering.

### 4. Generality of Results

The discontinuity across the cut in  $F_{2\gamma}(s_0, t)$  starting at  $t=0$  is proportional to the integral over the two-photon phase space of the product of the on-shell amplitudes  $A_1$  and  $A_2$ , where

$$A_i \equiv T_{i+\bar{i} \rightarrow \gamma+\gamma'}.$$

If we regard  $A_i$  as a function of the invariant energy  $t = (p_i + \bar{p}_i)^2$  and momentum transfer  $\sigma_i = (p_i - q)^2$ , we can expect that  $A_i = A_i(t, \sigma_i)$  will satisfy a dispersion relation in  $\sigma_i$ :

$$A_i(t, \sigma_i) = - \frac{1}{\pi} \int_{\bar{\sigma}_i}^{\infty} \frac{[A(t, \sigma_i')]}{\sigma_i' - \sigma_i} d\sigma_i', \quad (5.2)$$

spin labels being suppressed. For  $t < 0$ ,  $A_i$  represents the amplitude for Compton scattering by "i." If we reserve the integration over  $\sigma_i'$ , we recover the expression (2.12) for  $\rho_{2\gamma}$  on identifying  $M_s^2$  with  $\sigma_1'$  and  $M_i^2$  with  $\sigma_2'$ . Thus, the full  $\rho_{2\gamma}^{\text{irr}}(t)$  corresponds to a superposition of the diagrams typified by Fig. 4 and the rather general nature of our model becomes clear. [We have ignored subtractions in (5.2) as well as a term obtainable by replacing  $\sigma_i$  by  $\bar{\sigma}_i = (p_i - q')^2 = 4m^2 - t - \sigma_i$  on the right-hand side of (5.2). Inclusion of this term would generate contributions to  $\rho^{\text{irr}}(t)$  corresponding to those arising from diagrams obtained by crossing the photon lines in Fig. 4. These may be analyzed as in Sec. II and have analogous second-sheet singularities.]

However, it must be emphasized that in this paper we have regarded the Compton amplitude  $A_i$  as given to all orders in strong interactions but only to *lowest order in e*. For the case of elementary-particle scattering the meaning of this statement is clear and an

immediate consequence is that

$$\bar{\sigma}_i > M_i^2, \quad (i=1, 2) \quad (5.3)$$

if “ $\gamma$ ” is stable. In this approximation we then expect, as in the model, that  $\rho_{2\gamma}^{\text{irr}}(t)$  is an analytic function of  $t$  for

$$|t| < \min_{i=1,2} (\bar{\sigma}_i - M_i^2) / \bar{\sigma}_i.$$

For the case of atomic (e.g., hydrogen) scattering, the phrase to “lowest order in  $e$ ” must be understood as referring to photon emission and absorption *apart* from that which is to be regarded as giving rise to the vertex function for the virtual process

$$H \rightarrow e + p. \quad (5.4)$$

The hydrogen atom, of course, owes its very existence to electromagnetic forces and its wave function, and correspondingly the vertex function for (5.4) cannot be treated in perturbation theory.

From the present point of view, the calculation of CP corresponds to an approximation in which the elastic unitarity cut of the amplitude for  $\gamma + H \rightarrow \gamma + H$ , starting at  $\sigma = M_H^2$ , is replaced, for  $\sigma < (M_e + M_p)^2$ , by an (infinite) sequence of poles. These correspond to the very narrow resonances in  $\gamma$ -H scattering, usually called the excited states of hydrogen. Since the width of these levels is neglected, the first excited state is sharply removed in energy from the ground state and the equivalent of Eq. (5.3) obtains.

### 5. Concluding Remarks

We have seen that the nature of the one-photon and two-photon exchange forces between neutral spinless systems can be related to and understood in terms of the analyticity properties of the spectral function  $\rho(t)$ . These properties are in turn closely related to the structure of the colliding particles, as seen by one or more photons. For the case of two photons, all previous work on this subject, as well as the present work, has implicitly assumed that the two-photon probe may be regarded as weak, in the sense described in Sec. V B4.

Now although this would certainly seem to be a good approximation from a numerical point of view, it falsifies slightly the singularity structure of the spectral function  $\rho_{2\gamma}(t)$ . For, in the “weak-probe” approximation, the Compton amplitude  $i + \gamma \rightarrow i' + \gamma'$  does not satisfy elastic unitarity and correspondingly has a cut in the energy  $\sigma_i$  starting at  $\bar{\sigma}_i > M_i^2$ . This leads to a  $\rho_{2\gamma}(t)$  analytic in a neighborhood of  $t=0$  and to the universal  $R^{-7}$  behavior. However, if the elastic branch point at  $\sigma_i = M_i^2$  is kept,  $\rho_{2\gamma}(t)$  develops a singularity at  $t=0$  and the asymptotic behavior may be modified unless cancellations occur, e.g., as a result of 3-photon exchange. One would, of course, expect such effects to

be extremely small,<sup>14</sup> but this point may deserve further exploration. Another interesting problem is the question of what influence terms corresponding to the exchange of an arbitrary number of photons would have. Perhaps these can be summed in the neighborhood of  $t=0$ .

Finally, we remark that some of the equations and considerations one encounters in the covariant dispersion-theory approach to photon exchange forces bear eerie resemblance to those met in the currently popular game called current algebra. This similarity arises from the need to deal with scattering amplitudes continued to zero values of some external masses and from the important role played by 4-vector currents and (massive) vector particles; the photon, of course, is a nonfictitious zero-mass vector particle. It may well be that there are some further insights to be gained by studying amplitudes for processes involving photons which can be applied to those involving fictitious zero-mass particles.<sup>15</sup>

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### APPENDIX

It was stated above that certain second-sheet singularities of  $F(s_0, t)$  are “responsible” for the change from the  $R^{-7}$  behavior for  $R \gg b$  to the  $R^{-6}$  behavior for  $a \ll R \ll b$ , of the two-photon exchange potential  $V_{2\gamma}(R)$ . This assertion is supported and made more precise as follows. We divide the integration in Eq. (2.3) into the intervals I  $\equiv (0, t_1)$  and II  $\equiv (t_1, \infty)$ , where  $t_1 > 0$  is the first singularity of  $F(s_0, t)$  on the positive real  $t$  axis, and write

$$V \propto V_I + V_{II}, \quad (A1)$$

with

$$V_I = \frac{1}{R} \int_0^{t_1} \rho_I(t) e^{-(\surd t)R} dt, \quad (A2)$$

$$V_{II} = \frac{1}{R} \int_{t_1}^{\infty} \rho_{II}(t) e^{-(\surd t)R} dt. \quad (A3)$$

Here,  $\rho_I(t)$  denotes the spectral function  $\rho(t)$  in the interval  $(0, t_1)$  as well as its analytic continuation to complex  $t$  [see Eq. (2.14)]; note that  $t_1$  is necessarily a singularity of  $\rho_I(t)$ , so that  $\rho_I(t \pm i0)$  for  $t > t_1$ , obtained by analytic continuation from  $0 < t < t_1$ , is *not* equal to  $\rho_{II}(t)$ .

<sup>14</sup> For example, if  $\rho(t) \approx t^2 [1 + O(\alpha)(tL)^n \ln(tL^2)]$ , where  $L$  is a length, there is no modification of Eq. (1.1) at all if  $n > 0$ . For  $n = 0$ , Eq. (1.1) is modified, but only at distances which are large even by astronomical standards. For  $n$  sufficiently negative, there would be an appreciable effect if, say,  $L \sim b$ .

<sup>15</sup> A good illustration is given by S. Adler and Y. Dothan, Phys. Rev. **151**, B1267 (1966).

Suppose now that  $\rho_I(t)$  has no singularities in the entire open disk  $|t| < t_1$ ; then we may write the convergent expansion

$$\rho_I(t) = t^N \sum_{n=0}^{\infty} C_n t^n, \quad |t| < t_1 \quad (A4)$$

allowing for a zero of order  $N$  at  $t=0$ . From (A2) and (A4), it then follows that

$$V_I(R) = \frac{2}{R} \left( \frac{-\partial}{\partial R} \right)^{2N+1} \sum_{n=0}^{\infty} C_n \left( \frac{-\partial}{\partial R} \right)^{2n} \left( \frac{1 - e^{-(\sqrt{t_1})R}}{R} \right), \quad (A5)$$

which can be rewritten as

$$V_I(R) = \frac{1}{R^{2N+3}} \sum_{n=0}^{\infty} \frac{C'_n}{R^{2n}} \times \left[ 1 - e^{-(\sqrt{t_1})R} \sum_{j=0}^{2N+2n+1} \frac{(R\sqrt{t_1})^j}{j!} \right], \quad (A6)$$

where

$$C'_n = 2C_n(2N+2n+1)!$$

From (A3) it follows that, for a wide class of  $\rho_{II}(t)$ , e.g., for  $\rho_{II}(t)$  such that

$$A \equiv \int_{t_0}^{\infty} |\rho_{II}(t)| dt < \infty, \quad (A7)$$

we have, for all  $R$ ,

$$|V_{II}(R)| < (A/R)e^{-(\sqrt{t_1})R}. \quad (A8)$$

We specialize now to  $V_{2\gamma}(R)$  and to the case of atom-atom scattering, in particular to H-H scattering, so that  $N=2$  and

$$\sqrt{t_1} \approx 2a_0^{-1}. \quad (A9)$$

Then (A6) exhibits  $V_I(R)$  as a sum of terms involving inverse powers of  $R$ , powers lower than  $R^{-7}$  occurring only when accompanied by the rapidly decreasing exponential  $\exp(-2Ra_0^{-1})$ ; the latter also controls the decrease of  $V_{II}$ , as seen from (A8).

The preceding discussion shows that one cannot expect a dominant  $R^{-6}$  behavior in an appreciable region unless  $\rho_I(t)$  has singularities for  $|t| < t_1$ . However, the mere existence of such singularities is by itself not enough to ensure the precise behavior in question. In fact, what is really more directly relevant is what might be called the "medium-energy" behavior of  $\rho_I(t)$ ; by this we mean the behavior of  $\rho_I(t)$  in the interval  $(T, t_1)$ , where  $T$  is such that

$$\rho_I(t) \approx (\text{const})t^2, \quad (0 \leq t \lesssim T) \quad (A10)$$

but for  $t \gg T$ , Eq. (A10) ceases to be a good approximation. In particular, suppose that

$$\rho_I(t) \approx (\text{const}')t^{N'}, \quad (T \lesssim t \lesssim t_1) \quad (A11)$$

where  $N'$  is, for simplicity, an integer or half-integer. Then,

$$\frac{1}{R} \int_T^{t_1} \rho_I(t) e^{-(\sqrt{t})R} dt \approx \frac{(2 \text{const}')}{R} \left( \frac{-\partial}{\partial R} \right)^{2N'+1} \times \left[ \frac{e^{-(\sqrt{T})R} - e^{-(\sqrt{t_1})R}}{R} \right]. \quad (A12)$$

For

$$t_1^{-1/2} \ll R \ll T^{-1/2}, \quad (A13)$$

the right-hand side of (A12) is approximately

$$\frac{(2 \text{const}')}{R} \left( \frac{-\partial}{\partial R} \right)^{2N'+1} \frac{1}{R} \propto \frac{1}{R^{2N'+3}}.$$

Thus, for  $N' = \frac{3}{2}$  the contribution to  $V_I(R)$  from the interval  $(T, t_1)$  is approximately proportional to  $R^{-6}$ , in the domain (A13). To see that this contribution can indeed dominate that from the interval  $(0, T)$ , we consider a very crude model for  $\rho_I(t)$ , call it  $\rho_{I'}(t)$ , obtained by taking (A10) and (A11) as exact and assuring continuity at  $t=T$ :

$$\rho_{I'}(t) = \begin{cases} t^2 & (0 \leq t \leq T) \\ (\sqrt{T})t^{3/2} & (T \leq t \leq t_1). \end{cases} \quad (A14)$$

Then,

$$V_{I'}(t) \rightarrow \frac{-2}{R} \left( \frac{\partial}{\partial R} \right)^4 \times \left[ \frac{1 - e^{-(\sqrt{T})R} - (\sqrt{T})R e^{-(\sqrt{t_1})R}}{R^2} \right]. \quad (A15)$$

For  $R \gg T^{-1/2}$ , both the exponential terms in (A15) can be dropped and  $V_{I'} \approx R^{-7}$ , but in the interval (A13), the quantity in square brackets in (A15) is approximately  $T^{1/2}R^{-1}$ , so that  $V_{I'} \approx (\text{const})/R^6$  in this region.

Although the cancellation mechanism is very transparent with the model (A14), in detail it is misleading because of the presence of the "small" exponential  $\exp[-(\sqrt{T})R]$  in (A15) (see also Ref. 10); this arises from the nonanalytic nature of  $\rho_{I'}(t)$  in the neighborhood of  $t=T$ . However, the shift from  $t^2$  to  $t^{3/2}$  can be accomplished by a function which is analytic in a region containing the interval  $(0, t_1)$ . An example is

$$\rho_I(t; \kappa) \equiv t^2 [\tan^{-1}(t^{1/2}/\kappa)] / (t^{1/2}/\kappa). \quad (A16)$$

An even simpler example is provided by the function

$$t^2(\kappa^2 + t)^{-1/2}. \quad (A17)$$

The crossover point  $T$  for these examples is

$$T \approx \kappa^2,$$

so that, characteristically, the transition from  $t^2$  to  $t^{3/2}$  is "bought" by the introduction of a singularity at

$$t \approx -\kappa^2;$$

if we are to have  $T < t_1$ , then this singularity must be

inside the disk  $|t| < t_1$ , in agreement with the previous general analysis. The two examples show, on the one hand, that the precise nature of the singularities is not crucial for obtaining the  $R^{-7}$  to  $R^{-6}$  changeover, the singularity being logarithmic in (A16), but of the inverse square-root type in (A17). On the other hand, an arbitrary singularity structure is not permitted either. For example, a simple pole, i.e.,  $\rho_I(t) \propto t^2/(t+\kappa^2)$ , gives  $V_I \approx R^{-6}$  in the interval (A13), corresponding to the fact that now  $\rho_I \approx t$  for  $t \gg \kappa^2$ .

In summary, the  $R^{-6}$  dominance is tied to the existence of one or more left-hand singularities of  $\rho_I(t)$ . If we denote the nearest left-hand branch point by  $t_L$  ( $< 0$ ) and neglect possible complex singularities of  $\rho_I(t)$ , we may write

$$\rho_I(t) \propto t^2 \Phi(t), \quad (\text{A18})$$

with

$$\Phi(t) = \frac{1}{2\pi i} \int_{-\infty}^{t_L} \frac{[\Phi(t')]}{t'-t} dt' + \frac{1}{2\pi i} \int_{t_1}^{\infty} \frac{[\Phi(t')]}{t'-t} dt'. \quad (\text{A19})$$

If the discontinuity  $[\Phi(t)]$  for  $t \leq t_L$  is such that the first term in (A19) is  $O(1)$  for  $0 \leq t \lesssim -t_L$ , and is  $O[(-t_L/t)^{1/2}]$  for  $-t_L \ll t \ll t_1$ , one expects  $R^{-6}$  dominance in the interval

$$t_1^{-1/2} \ll R \ll (-t_L)^{-1/2},$$

provided that the second term in (A19) can be neglected. Such a neglect seems plausible in the atomic case, where it is related to the validity of the dipole approximation for single-photon emission.

The functions defined by Eqs. (A16) and (A17) both provide examples of  $\rho_I$  in which the second term in (A19) is in fact absent. The functions  $\rho_{m,n}(t)$  and  $\rho_{m,m}(t)$ , Eqs. (3.3) and (3.4), obtained by transformation of the CP formula provide more physical examples; the singularity at  $t_1$  is absent again because the dipole approximation has been made. The covariant calculation of Sec. II gives rise to such a term if the structure of the vertex  $V_{(1)\alpha\mu}$  [Eq. (2.9)] is taken into account.

The above discussion suggests that one define a sort of prototype potential  $V_I(R; \kappa)$  by

$$V_I(R; \kappa) = \frac{(\text{const})}{R} \int_0^{t_1} \rho_I(t; \kappa) e^{-(\surd t)R} dt, \quad (\text{A20})$$

where  $\rho_I(t; \kappa)$  is defined by Eq. (A16). A superposition

$$\int_{\kappa_{\min}}^{\infty} h(\kappa) \rho_I(t; \kappa) d\kappa$$

is then expected, on the basis of the analysis of Secs. II and III, to represent the dominant contribution to  $\rho_I(t)$  in an interval

$$\kappa_{\min}^2 \ll t \ll t_1.$$

Correspondingly, in an interval

$$t_1^{-1/2} \ll R \ll \kappa_{\min}^{-1},$$

$V_{2\gamma}(R)$  should be well represented by

$$\bar{V}_I(R) = \int_{\kappa_{\min}}^{\infty} h(\kappa) V_I(R; \kappa) d\kappa. \quad (\text{A21})$$

For  $\kappa \ll \sqrt{t_1}$  and  $R \gg (t_1)^{-1/2}$ , one may replace the upper limit in (A20) by infinity, to obtain

$$\begin{aligned} V_I(R; \kappa) \approx (\text{const}) \left( \frac{2\kappa}{R} \right) & \left[ \frac{24}{R^5} - \frac{12\kappa^2}{R^3} + \frac{\kappa^4}{R} \right] \\ & \times (\text{CikR} \sin \kappa R - \text{sikR} \cos \kappa R) \\ & - \left[ \frac{24\kappa}{R^4} - \frac{4\kappa^3}{R^2} \right] (\text{CikR} \cos \kappa R + \text{sikR} \sin \kappa R) \\ & + \left. \frac{18\kappa}{R^4} - \frac{\kappa^3}{R^2} \right\}. \quad (\text{A22}) \end{aligned}$$

It follows that for  $(t_1)^{-1/2} \ll R \ll \kappa^{-1}$

$$V_I(R; \kappa) \approx (\text{const}')/R^6. \quad (\text{A23})$$

The validity of (A23) leads one to expect that  $\bar{V}_I(R)$  will satisfy, for a wide class of  $h(\kappa)$ ,

$$\bar{V}_I(R) \approx (\text{const}'')/R^6$$

for

$$(t_1)^{-1/2} \ll R \ll \bar{\kappa}^{-1}.$$

Here  $\bar{\kappa}$  is a mean value of  $\kappa$ , determined by  $\kappa_{\min}$  and the falloff of the weight function  $h(\kappa)$  for large  $\kappa$ .

Our discussion, heuristic in part, may be useful in suggesting a rigorous approach to some questions which can be raised regarding the standard discussions of interatomic forces. In particular, we note that the argument which leads to the London potential (1.3) involves the interchange of the order of two operations:

- (i) summation over an infinite number of intermediate states in the expression for  $\Delta E_{cc}$  in terms of  $V_c$ ,
- (ii) replacing  $V_c$  by its dipole approximation, i.e. letting  $R$  become large.

To our knowledge, it has not been shown that interchanging the order of (i) and (ii) is really permissible.